Why interference tests?

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Why Interference Tests?

by

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Abstract

In neutron activation analysis, correction for interference from other elements is usually carried out in the data processing; this is, however, only feasible when the radio-nuclides in question have at least one significant peak that is interference-free.

Interference between nuclides with only one major photopeak and with comparable half-lives is best resolved by applying corrections based on experimentally determined values. In an extension of our previous method for the determination of As, Mn and Se to include Cu and Zn, interference from Cu in the determination of Zn is of this type. Furthermore, ^{64}Cu interferes not only with the ^{69m}Zn indicator used for determination of Zn in the separated sample, but also with the ^{65}Zn tracer added for chemical yield determination.

Tests of the accuracy of the method were carried out by analysis of Standard Reference Materials 1571, Orchard Leaves, and 1577, Bovine Liver, from the National Bureau of Standards. For Orchard Leaves and for most biological materials, the interference from Cu was below the limit of detection for Zn; for Bovine Liver and other materials with unusual trace concentrations, correction was applied by means of an iterative procedure.

Excellent agreement with certified values was finally obtained for both materials.

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Interference from other elements activated by thermal neutrons is a potential, but neglected source of error in neutron activation analysis. Numerical values for the interference are rarely included in the performance characteristics of activation analysis methods although, when assessing a method, it is essential to know the effect of an interfering element on a particular concentration of the element to be determined.

The main purpose of the experimental determination of interference is naturally to ascertain interference-free determination, but values for the interference can also be used to obtain unbiased results, provided that the test is properly designed and that the concentration of the interfering element is known.

To show this, I will use an example from a recent medical study[1].

In this study we needed a method for the simultaneous determination of arsenic, copper, manganese, selenium, and zinc. The obvious thing to do was to incorporate separation procedures for copper and zinc into our already existing method for the determination of arsenic, manganese and selenium in biological material[2].

Zinc is of special interest in this method because the determination of this element is not entirely interference-free.

The method calls for a one-hour irradiation at $7 \cdot 10^{12}$ neutrons/cm^2/sec of a one-gram sample followed by wet ashing and radiochemical separation during which zinc and manganese are extracted simultaneously. ^{69m}Zn is used as indicator, and the chemical yield is determined by added ^{65}Zn tracer.

It was desirable to keep the counting time at a minimum and to determine the zinc content from just one spectrum. Therefore, 24 hours after pile-out, the zinc sample is counted for 20 minutes in a well-type NaI(Tl)-detector. Counting on a Ge(Li)-detector would require 200 minutes to achieve a comparable precision.

Figure 1 shows a typical spectrum of a separated zinc sample. ^{65}Zn emits positrons giving rise to a small 511 keV annihilation peak which interferes with the 438 keV peak of the ^{69m}Zn indicator. Therefore, the peak area is first corrected for the contribution of ^{65}Zn by stripping of the 1115 keV peak by means of a spectrum of ^{65}Zn. The corrected area is then compared with that of a standard to obtain the amount of zinc in the separated sample. The chemical yield is determined from the 1115 keV peak which represents both the ^{65}Zn tracer and the ^{65}Zn formed during the irradiation. From the corrected 438 keV peak, the amount of zinc in the separated sample is known and the ^{65}Zn formed can be found from the spectrum of the comparator standard. The 1115 keV peak is corrected

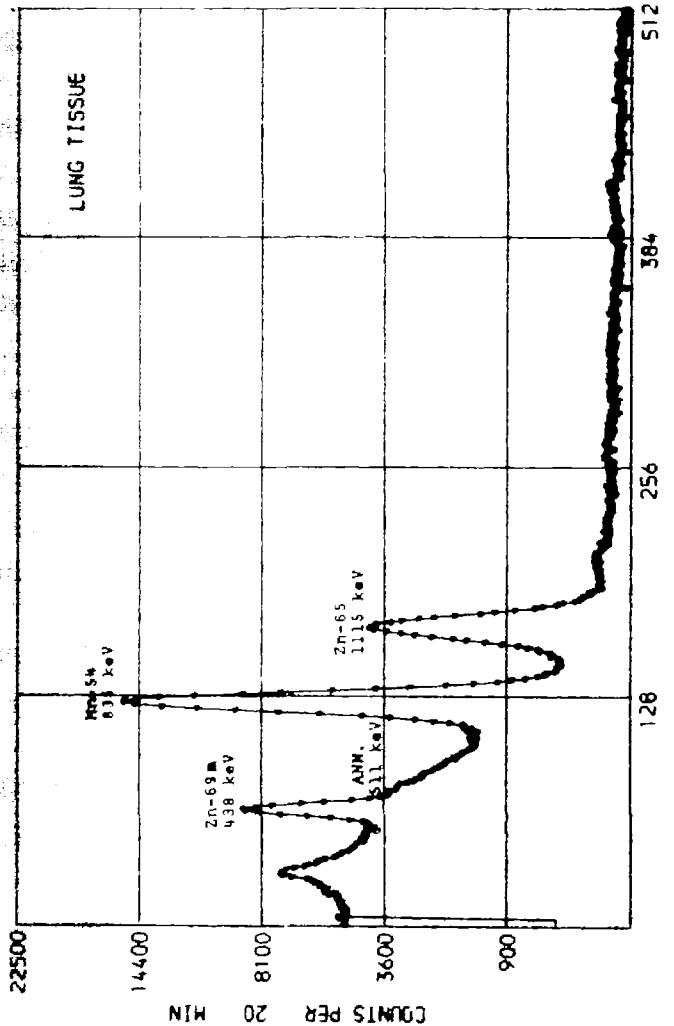

Fig. 1. Spectrum of separated zinc sample

for this contribution before calculation of the chemical yield and subsequent calculation of the zinc concentration in the sample.

The method was tested for interference from various elements. When the chemical yield is determined by added tracer, interference on both indicator and tracer is possible.

Our method for experimental determination of interference[2] consists of two steps (table I):

Table I

Determination of interference

Interference = $\frac{1}{S \cdot f}$	S = separation factor f = effective value
where $S = \frac{1}{D \cdot y}$	D = decontamination factor y = chemical yield
and $f_{indicator} = m^*/m$	m^* = apparent quantity m = quantity of interf. elem.
$f_{tracer} = \%/m$	% = relative error of yield

The first step is the determination of what is known as an effective value f for the indicator, which value is found by irradiating a known quantity m of the interfering element and counting it as a sample. By comparing with a standard of the element to be determined the apparent quantity m^* is found. f is expressed as µg of element/µg of interfering element.

The effective value for the tracer is found in a similar way by comparing with the specified amount of tracer. f then expresses the error in % of the yield/µg of interfering element.

The second step is the determination of a decontamination factor D. A radioactive tracer of high specific activity is added to an unirradiated sample. The sample is processed according to the procedure and the decontamination factor is then the ratio between the added and the recovered activity. The decontamination factor is corrected for chemical yield, which

should be close to that normally found, and its reciprocal, the separation factor S, can be calculated.

The interference can now be expressed as $\frac{1}{S \cdot f}$, which expresses the concentration that corresponds to an error of 1 ppm for interference on the indicator and to an error of 1% for interference on the chemical yield.

The results of our interference determination are shown in table 2.

Table 2

Result of interference determination

Interfering element	Indicator	Tracer
	ppm element ~ ± 1 ppm Zn	ppm element ~ ± 1% error
Na	500,000	100,000
Cu	40	30
Br	6,000	200

Very high values were obtained for sodium and bromine. Such concentrations are never found in biological material, and the contribution from these elements to the zinc result is well below the detection limit. However, copper concentrations of 30-40 ppm are not uncommon and copper may in such cases interfere significantly with the determination of zinc.

The interference on the zinc indicator is caused by the 511 keV annihilation peak of ^{64}Cu. The interference on the tracer is caused by the sum peak of 1.02 MeV, which is present in the spectrum because the sample is counted in a well-type detector.

Having found copper interference on both the indicator and the tracer, we have to find the total error. To do this we need the S · f value, which is 0.023 for the indicator, meaning that 1 ppm of copper causes an error of 0.023 ppm of zinc. For the tracer, 1 ppm of copper causes an error of 0.036% of the yield, and therefore also of the zinc concentration. The total error is then

$$\text{absolute error, ppm} = 0.023 \cdot Cu + 3.6 \cdot 10^{-4} \cdot Cu \cdot Zn$$

and

$$\text{relative error, \%} = 2.3 \cdot \frac{Cu}{Zn} + 0.036 \cdot Cu. \qquad (1)$$

From this equation we are able to calculate the error when the copper and zinc concentrations are known. For the Standard Reference Materials, Orchard Leaves and Bovine Liver, from the National Bureau of Standards, the errors are 1.5% and 10% respectively.

To decide whether a zinc result should be corrected for copper interference, we relate the error to the a priori detection limit calculated according to Currie[3]. Based on the standard deviation from counting statistics only, and using the lowest results among the tissue samples analyzed, we find a detection limit of 0.9 ppm of zinc[4]. A correction should then be applied when

$$\text{absolute error, ppm} \geq 0.9$$

or

$$\text{relative error, \%} \geq \frac{90}{Zn}. \qquad (2)$$

It is easier to comprehend the significance of equations (1) and (2) by looking at figure 2 where we have plotted a series of straight lines showing the relative error as a function of the zinc concentration for Cu/Zn ratios of 2, 1, 1/2, and 1/10. The error on the indicator determines the intersection with the ordinate axis, while the slope is determined by the error on the tracer.

The curve is the hyperbola described by the absolute error being equal to the detection limit. Tissue samples, except liver, are found in region B below the curve where no correction is necessary. A small correction of 1-3% is required for human liver samples in region A.

We tested the accuracy of the analytical method by analysis of the Standard Reference Materials Orchard Leaves and Bovine Liver. The copper and zinc concentrations in these materials place Orchard Leaves below and Bovine Liver above the curve.

Table 3 shows an uncorrected mean value of 23.9 ± 0.8 ppm for Orchard Leaves in good agreement with the certified value of 25 ppm[5].

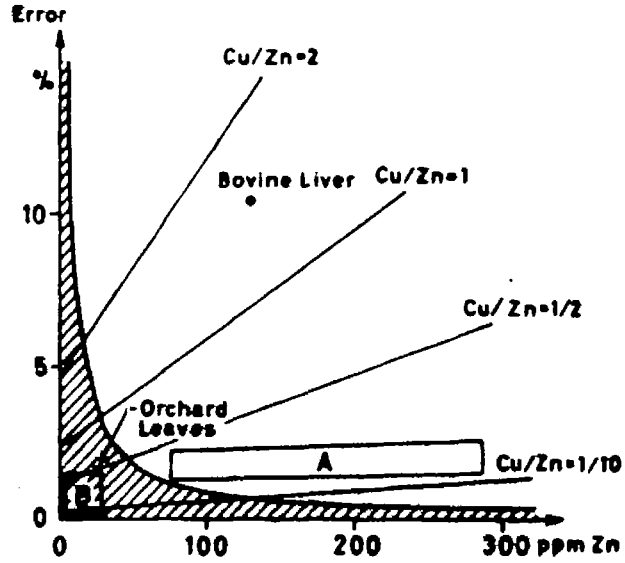

Fig. 2. Error versus Zn concentration for various Cu/Zn ratios
A Liver B Other biological materials analyzed

Table 3

Concentration of zinc in SRM 1571 Orchard Leaves

	Mean value ppm	Number of determinations
This work	23.9 ± 0.8	4
NBS	25 ± 3	certified

For Bovine Liver, where a correction for interference is necessary, two sets of requirements must be fulfilled:

1. The chemical yield must be normal for the separation factor as well as for the sample to be corrected.
2. The same peak boundaries must be used to calculate the effective values and the zinc result.

In this study we selected peak boundaries giving maximum precision[6] as opposed to the method in which boundaries are fixed from the sign change of the first derivative calculated from a third degree polynomial convolution of a smoothed spectrum[7].

Figure 3 shows a spectrum of a separated zinc sample of Bovine Liver. The sum peak from ^{64}Cu interferes with the ^{65}Zn tracer, and our experimentally determined value for interference is applicable to the tracer, but not to the total amount of ^{65}Zn. Therefore, the amount of zinc in the sample cannot be calculated as we do not know the correct amount of ^{65}Zn. Moreover, as we do not know the amount of Zn, we are also unable to calculate the chemical yield.

The solution to the problem is to use iteration involving the following steps:

1. Calculate the error on the indicator and the error on the tracer from the experimentally determined values for interference and the copper concentration.
2. Calculate the yield assuming that the 1115 keV peak area is due to ^{65}Zn tracer.
3. Correct the ^{69m}Zn peak area for interference from the annihilation peak of ^{65}Zn.
4. Calculate the amount of zinc in the separated sample and add the error on the indicator multiplied by the chemical yield.

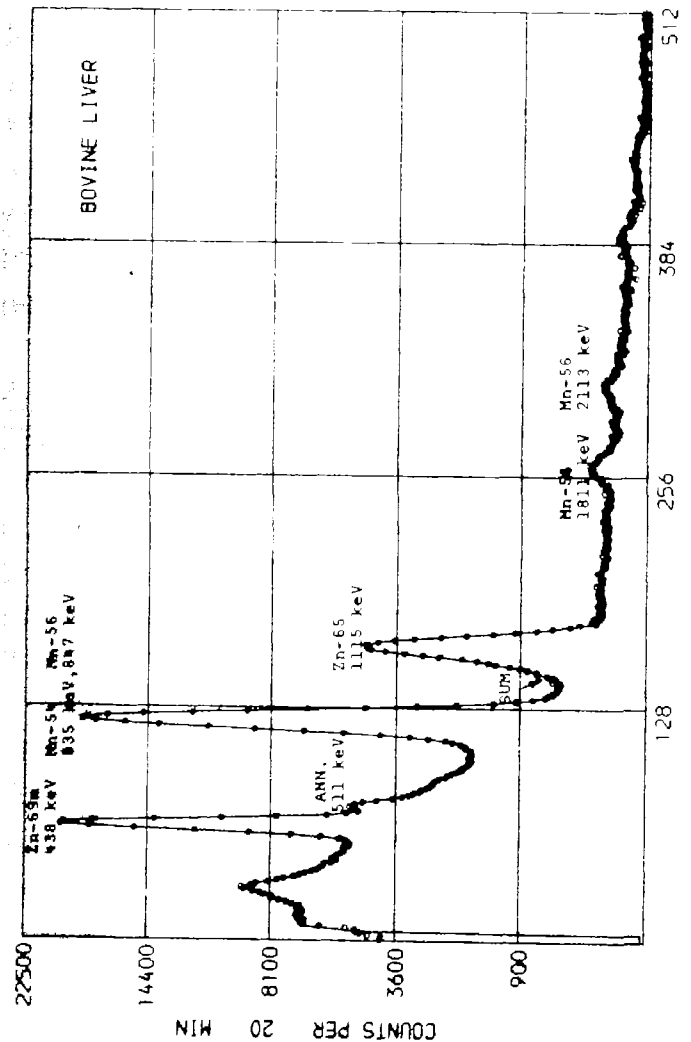

Fig. 3. Spectrum of separated zinc sample

5. Calculate the ^{65}Zn formed during irradiation.
6. Subtract the ^{65}Zn formed from the 1115 keV peak area and correct the difference for interference on the yield.
7. Calculate the ^{65}Zn in the sample.
8. Calculate the yield and the concentration.
9. Repeat steps 3 to 8 with the new values for ^{65}Zn and yield until the change in concentration is well below the detection limit.

The above differences are illustrated in table 4:

Table 4

Concentration of zinc in SRM 1577 Bovine Liver

Number of determinations	Mean value, ppm			NBS
	uncorrected		corrected	certified
11	118[1]	122[2]	129.5 ± 1.5	130 ± 10

Peak boundaries: 1. Sign change of first derivative[7)]
2. Maximum precision[6)]

First, we have the uncorrected mean value of 118 ppm calculated without accounting for interference and using peak boundaries determined by the sign change of the first derivative.

The second mean value of 122 ppm is found by using boundaries selected to give maximum precision.

The third and final value of 129.5 ± 1.5 ppm is the mean value corrected for interference by the iteration method. This value is in excellent agreement with the certified value of 130 ppm[8)]. The correction is only 6% because the sample size was reduced to less than one gram without reducing the tracer addition correspondingly.

This example shows clearly that the applicability of a neutron activation analysis method must be precisely specified, and that knowledge of interference is required to avoid quoting erroneous results.

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